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Optical Properties of Distyrylbenzene
Chromophores and Their Segmented Copolymers

by

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OPTICAL PROPERTIES OF DISTYRYLBENZENE CHROMOPHORES AND THEIR SEGMENTED COPOLYMERS.

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Abstract

A new segmented polymer (**3**) consisting of a distyrylbenzene chromophore separated by polyethylene glycol segments has been prepared by two independent methods: a novel, polymer analogous Mitsunobu reaction and conventional double displacement reaction. The polymer is soluble in a variety of organic solvents, forms excellent, optically clear films and exhibits strong fluorescence. The properties of the chromophore and the polymer, as well as the scope and limitations of the novel Mitsunobu polymerization are presented. Attempts to use polymer (**3**) in electroluminescent devices are also discussed.

Introduction

In recent years, poly(p-phenylenevinylene) (PPV) has been extensively investigated because it exhibits efficient photoluminescence and potentially useful electroluminescent properties.¹ Numerous phenylene vinylene oligomers have been synthesized in order to improve the solubility and stability of these materials as well as to tune their emission frequencies.^{2,3,4,5,6,7,8,9} In a light-emitting electrochemical cell (LEC), emission occurs because of hole-electron combination, from electrochemically generated p-type and n-type materials. In this case, good counterion mobility is required. This concept has been used to fabricate numerous devices using poly(ethylene glycol), as the ion transporting medium blended with a photoluminescent material.¹⁰ A potential problem with this approach has been phase separation of a hydrophobic chromophore and the oligo(ethylene glycol).¹¹ Only one other electroluminescent polymer, in which diethylene glycol units are attached as side chains on a oligo(p-phenylene) backbone, has so far been reported.¹²

Here we report the first synthesis of a polymer containing a photoluminescent distyrylbenzene chromophore separated by poly(ethylene

glycol) spacers. This polymer exhibits efficient solution fluorescence and was characterized by ^1H NMR, ^{13}C NMR, IR, elemental analysis, X-ray powder diffraction, TGA and DSC.

EXPERIMENTAL SECTION

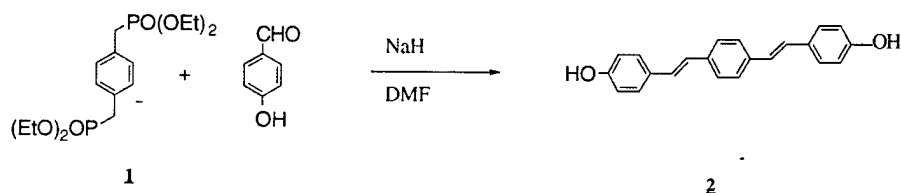
Materials. All solvents and materials were used as received unless otherwise noted. α, α' -Para xylylene dichloride and polyethylene glycol were purchased from Aldrich. Poly(ethylene glycols) were dried at 45°C under vacuum over P_2O_5 for a minimum of three days. Tetrahydrofuran (THF) was distilled from sodium under inert atmosphere. All reactions were performed under a dry argon atmosphere.

Chromophore. The distyrylbenzene chromophore (**2**) was synthesized by direct condensation of the bis phosphonate (**1**) with p-hydroxybenzaldehyde using excess sodium hydride in DMF (Scheme 1).¹³

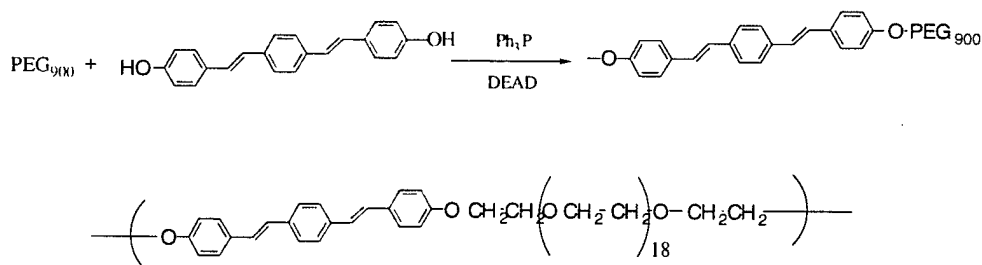
The expected all trans configuration was confirmed by ^1H NMR and IR spectroscopy.¹⁴ The chromophore itself is a yellow, crystalline material, very sparingly soluble in most organic solvents at room temperature. It exhibits a fluorescence in the solid state and even very dilute solutions exhibit an extremely strong blue fluorescence (0.188 g/L, $\lambda_{\text{max}} = 395 \text{ nm}$).

Scheme 1

Synthesis of a PPV-PEG Copolymer



Mitsunobu Polymerization



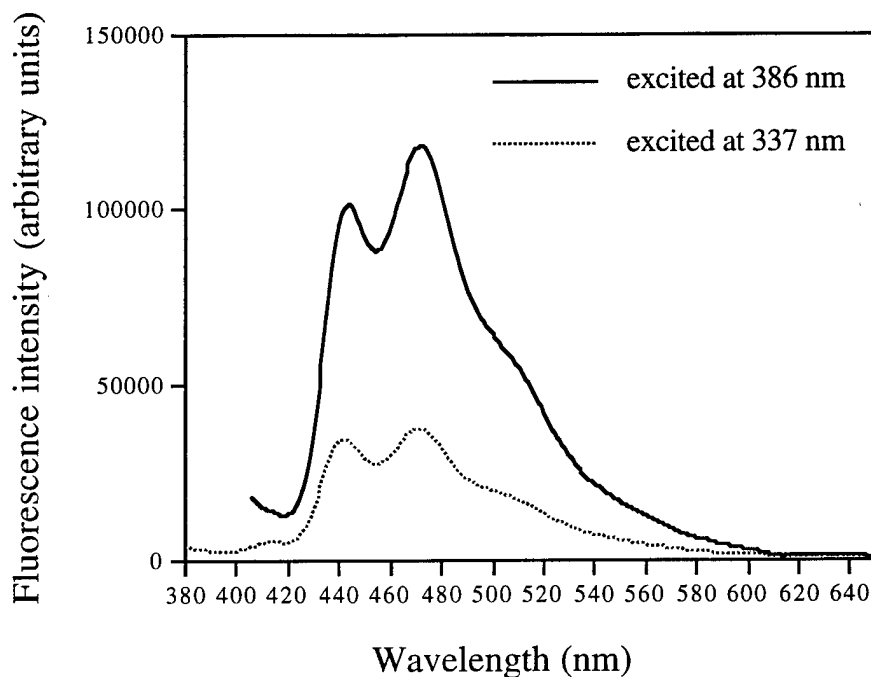


Figure 1. Emission spectra. Both spectra have peaks at 443nm and 471nm.

Polymer. The commercially available PEG that was used in this study (Mn 900, Pd 1.1) corresponds to approximately twenty ethylene glycol units. Polycondensation of the distyrylbenzene segment (**2**) with poly(ethylene glycol) was initially carried out via a Mitsunobu reaction and are the first examples of what seems to be a new and useful polymerization method^{15,16} Upon addition of diethyl azodicarboxylate (DEAD) to a suspension of the chromophore to a solution of poly(ethylene glycol) and triphenyl phosphine in THF at 45°C, the chromophore slowly dissolves. Extended heating over 2 days gave a viscous solution. Precipitation into ethanol and drying under vacuum over P₂O₅ gives the desired polymer as a yellow rubbery powder in 90% yield.

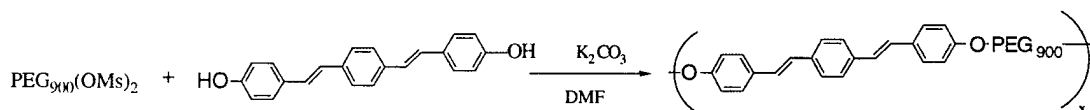
RESULTS AND DISCUSSION

To our knowledge, this is the first example of the use of the Mitsunobu reaction to carry out a condensation polymerization. We have used this reaction to also prepare a number of end functionalized poly(ethylene glycols) and poly(ethylene glycol) copolymers that we will report in subsequent publications. It should be noted, however, that large significant IR absorptions at 1740 and 1700 cm⁻¹ are indicative of carbonyl groups. Together with elemental analyses and comparison to the IR spectrum of diethylhydrazine dicarboxylate in the 1700 to 1800 cm⁻¹ region, the incorporation of hydrazino carboxylate residues in the Mitsunobu prepared polymer was indicated. Preparation of a sample by

an alternate route (Scheme 2) from poly(ethylene glycol) bis(mesylate)¹⁷ gave a product with no absorptions in the carbonyl region.

Scheme 2

Alternate Polycondensation



The polymer is soluble in THF, DMF, chloroform and acetonitrile. In addition, the lack of any detectable peak at 4.56 ppm indicated <1.0% of ethylene glycol end groups.¹⁸ The ratio of peaks from the chromophore to those from the ethylene glycol segment is also in good agreement with a 1:1 copolymer. The known insolubility of the chromophore suggested that we have a reasonably high molecular weight product. Size Exclusion Chromatography (SEC) analysis of the polymer in chloroform gave good agreement with commercially available PEG samples and indicates a clean monomodal distribution with M_n 7400, M_w 18,700, P_d 2.5. The peak molecular weight is 10,800 and corresponds to a DP of 9.

The polymers synthesized were investigated for their fluorescence properties. In DMF solution, when excited in the wavelength range 320-400 nm, the polymer exhibited strong fluorescence in the range 410-470 nm. When pumped with a 337 nm nitrogen 3 nsec laser pulse, a solution of the polymer exhibited laser action due to the amplified spontaneous emission. The intensity of this laser action is comparable when only the chromophore at comparable number densities was used. This clearly establishes that the chromophore does not have any significant loss in quantum efficiency when incorporated into polyethylene oxide segments. The absorption spectrum of a spin coated film (1129 Å) has a maximum at 318 nm. The fluorescence spectra of a cast film on a quartz substrate is shown in Figure 1. The structure observed in both absorption and fluorescence emission spectra is attributed to vibronic effects and has a frequency separation of approximately 1300 cm^{-1} . A thin film of the polymer also showed very strong fluorescence and experiments to establish evidence of stimulated emission when pumped in the UV are in progress.

Thermal Properties.

The thermogravimetric analyses (TGAs) of the polymer in air and under N₂ show a gradual weight loss above 50°C, 98.18% of the material is still present at 258°C and nearly 95% at 336°C (under N₂). Mates and

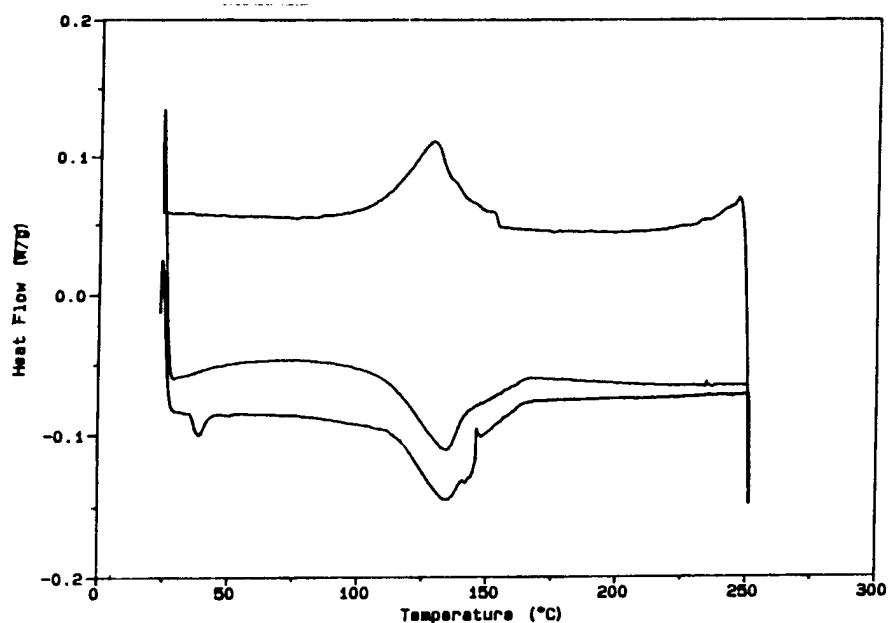


Figure 2 DSC of the Polymer (3)

Ober¹⁹ prepared a number of alkyl derivatives of the same chromophore and showed that several of them demonstrated liquid crystalline behavior. The DSC trace (Figure 2) shows a transition at approximately 55°C which is not observed in subsequent traces. This indicates a possible liquid crystalline transition.

Device Experiments

We have made several attempts to incorporate (3) into a light-emitting device. Attempts to use (3) in a LEC have not been successful to date. On top of a spin coated film of (3) on an indium tin oxide (ITO) slide was coated a layer (300-400 Å) of a sulfonated tris-phenanthroline Ru^{+2} complex that has been previously used in light emitting devices.²⁰ Red orange light similar to that previously reported is obtained in these devices at voltages up to +6 volts with a luminance of 40 candelas/m². The current density at this voltage is 50 ma/cm². Use of higher voltages led to irreversible malfunctioning of the devices.

CONCLUSIONS

We have prepared a novel PPV analog containing a known ion transport moiety (PEG) by both a novel Mitsunobu reaction and by a convention double displacement reaction. The polymer was fully characterized and is easily processible yielding optically clear, highly fluorescent films. Laser action has been observed in solution. Studies of light emitting devices using (3) have been initiated.

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